UTS UNIVERSITY OF TECHNOLOGY SYDNEY

# IMMOBILIZATION OF NANOSCALE ZERO-VALENT IRON (NZVI) ONTO ELECTROSPUN NANOFIBER MEMBRANE FOR GROUNDWATER REMEDIATION

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**Doctor of Philosophy**

under the supervision of Hokyong Shon and Leonard Tijing

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# CERTIFICATE OF ORIGINAL AUTHORSHIP

I, Jiawei Ren, declare that this thesis, is submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the School of Civil and Environmental Engineering, Faculty of Engineering and Information Technology at the University of Technology Sydney. This thesis is wholly my own work unless otherwise reference or acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis. This document has not been submitted for qualifications at any other academic institution.

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**Book chapters and Journal Articles Published or Submitted****

<u>** Publications made during the PhD candidature related to the Thesis.*</u>

[1] ****<u>J. Ren</u>***, M. Yao, L.D. Tijing, H.K. Shon, Hierarchical immobilization of nZVI onto electrospun PVA-PAA nanofiber membrane via layer-by-layer method for long-term gravity-driven microfiltration, Composites Part B: Engineering, under revision.

[2] ****<u>J. Ren</u>***, M. Yao, L.D. Tijing, H.K. Shon, NZVI immobilization onto electrospun PVDF-GO membrane for groundwater remediation via gravity-driven membrane filtration, Science of the Total Environment, 688 (2019): 787-796

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**Conference papers and presentation**

[1] ***J. Ren***, Y. Woo, L.D. Tijing, H.K. Shon, Hierarchical Immobilization of nZVI onto Electrospun PVA-PAA Nanofiber Membrane for Groundwater Remediation. (***Sept. 2019, CleanUp 2019 – the 8th International Contaminated Site Remediation Conference, Adelaide, Australia***)

[2] ***J. Ren***, Y. Woo, L.D. Tijing, H.K. Shon, NZVI Immobilization onto Electrospun Nanofiber Membrane for Groundwater Remediation via Multiple Dip-Coating Method. (***Sept. 2019, Chemeca 2019, Sydney, Australia***)

[3] ***J. Ren***, Y. Woo, L.D. Tijing, H.K. Shon, Green Synthesis and Immobilization of Nanoscale Zero-Valent Iron (nZVI) onto the Electrospun PAA-PVA Membrane. (***Aug. 2019, ICNST 2019, Incheon, Korea***)

[4] ***J. Ren***, L.D.Tijing, H.K.Shon, Effect of polymer ratio on nZVI loading onto Electrospun nanofiber membrane for mitigating groundwater contaminants, Advanced Materials-TechConnect Briefs 2017. (***May 2017, Nanotech 2017, Washington D.C, USA***)

[5] ***J. Ren***, Y. Woo, L.D. Tijing, H.K. Shon, Mechanical strength enhancement of nZVI-immobilized electrospun nanofiber membrane for groundwater remediation. (***July 2018, AMS 11, Brisbane, Australia***)

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*Presentation made during the PhD candidature including proceedings, oral and poster presentations.*

## LIST OF ABBREVIATIONS

| | |
|---|---|
| AOPs | Advanced Oxidation Processes |
| ATR-FTIR | Attenuated Total Reflectance–<br>Fourier Transform Infrared Spectroscopy |
| ATRP | Atom Transfer Radical Polymerization |
| BET | The Brunauer-Emmett-Teller |
| BSA | Bovine Serum Albumin |
| CA | Contact Angle |
| $Cd\ (NO_3)_2$ | Cadmium Nitrate |
| –COOH | Carboxyl Group |
| CT | Tetrachloride |
| $Cu\ (NO_3)_2$ | Cupric Nitrate |
| DI | De-Ionized |
| DMF | N, N-Dimethylformamide |
| DO | Dissolved Oxygen |
| EDX | Energy Dispersive X-Ray Spectroscopy |
| ENM | Electrospun Nanofiber Membrane |
| EPA | Environmental Protection Agency |
| Fe(II) | Ferrous Ions |
| Fe(III) | Ferric Ions |
| $FeCl_3$ | Ferric Chloride |
| $FeSO_4 \cdot 7H_2O$ | Sulphate Heptahydrate |
| GO | Graphene Oxide |
| $H_2O_2$ | Hydrogen Peroxide |

| | |
|---|---|
| ISCO | In-Situ Chemical Oxidation |
| IWA | In-Well Aeration |
| MF | Microfiltration |
| MW | Molecular Weight |
| $NaBH_4$ | Sodium Borohydride |
| NaOH | Sodium Hydroxide |
| NOMs | Natural Organic Matters |
| nZVI | Nanoscale Zero-Valent Iron |
| P&T | Pump And Treat |
| PAA | Polyacrylic Acid |
| PAN | Polyacrylonitrile |
| PCBs | Polychlorinated Biphenyls |
| PCE | Tetrachloroethylene |
| PGMA | Poly(Glycidyl Methacrylate) |
| PRB | Permeable Reactive Barrier |
| PSD | Pore Size Distribution |
| PVA | Polyvinyl Alcohol |
| PVDF | Polyvinylidene Fluoride |
| RH | Relative Humidity |
| SEM | Scanning Electron Microscopy |
| TCD | *Tip-To-Collector-Distance* |
| TCE | Trichloroethylene |
| TEM | Transmission Electron Microscopy |

| | |
|---|---|
| TGA | Thermogravimetric Analysis |
| $TiO_2$ | Titanium Oxide |
| UF | Ultrafiltration |
| XRD | X-Ray Diffraction |
| $\alpha$-$Fe_2O_3$ | Hematite |
| $\alpha$-FeOOH | Goethite |

# ABSTRACT

Nanoscale zero-valent iron (nZVI), as a promising material, has been widely used in groundwater remediation. However, individual nZVI particles are prone to agglomeration and hence sediment in the water environment, which reduces the reactivity of nZVI as well as its performance in contaminant removal. Membrane-supported nZVI can both avoid nZVI agglomeration for better reactivity and recycle nZVI/contaminants to lower the risk of secondary pollution.

In this study, a new approach that combines nZVI with electrospinning technology has been put forward to obtain the membrane-supported nZVI. First, we developed a polyacrylic acid - polyvinyl alcohol (PAA-PVA) electrospun nanofiber membrane. The results indicate that nZVI particles were successfully immobilized on the membrane and had excellent removals to methylene blue and Cu (II) ions at 94% and 83.6% respectively. Subsequently, a “robbing behaviour” was observed during the nZVI immobilization. The robbing behaviour can significantly reduce the number of nZVI particles immobilized onto the membrane and hence weaken the performance of mitigating contaminated water. To minimize the undesirable effect of robbing behaviour, we developed a dipping method that enables exposure of enough free Fe (II) as electron acceptors to the Fe (II)-complexed PAA-PVA membrane for the subsequent reduction. The results shows that the membrane with dipping can immobilize more than 1.7 times the weight percentage of nZVI particles for the membrane without dipping. However, we found that the developed PVA-PAA-nZVI composites had a low mechanical strength after undergoing multiple reduction by $NaBH_4$ and membrane mechanical strength is a critical property for a long-term operation and the regeneration of nZVI membranes. Therefore, a high molecular weight dualcrosslinking method was investigated to improve the mechanical strength of polymeric electrospun nanofiber membranes.

Alternatively, we examined to fabricate a polyvinylidene fluoride - graphene oxide (PVDF-GO) nanofiber membrane composite for nZVI immobilization. The addition of GO into PVDF nanofibers can both increase the hydrophilicity to improve membrane flux and offer –COOH as a binder to immobilize nZVI particles. PVDF-GO-nZVI membranes with different GO loadings (0%, 0.5%, 1%, 3% of PVDF) were tested with two typical nZVI-targeted contaminants (Cd(II) and trichloroethylene (TCE)) via gravity-driven membrane filtration. The results show that membrane with 1% GO had the best nZVI distribution against the aggregation and a better performance in both Cd removal (100%) and TCE removal (82%).

To sum up, the eletrospun nanofiber membrane is a very suitable material for nZVI immobilization and the developed nZVI-immobilized electrospun nanofiber membrane composites had a great potential in groundwater remediation.

**Keywords**: nZVI; Electrospun nanofiber membrane; Membrane-supported nZVI; Groundwater remediation; Gravity-driven membrane filtration; Immobilization; Nanoparticles; Electrospinning; Composites

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